

Sintering of bioceramics using a modified domestic microwave oven

Natural hydroxyapatite sintering

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Abstract In this study, hydroxyapatite (HA) prepared from calcined bovine bone was studied. Two methods were used for HA sintering: conventional sintering (CS) and microwave sintering (MS). HA was obtained by calcination of bovine bone at 800 °C for 4 h followed by wet ball milling. Afterwards, the powder was compacted under 75 MPa and sintered for 2 h at different temperatures, from 1050 to 1200 °C. It has been found that the bulk density of HA increases by increasing sintering temperature when both CS and MS were used. Nevertheless, at the same temperature and for a shorter time (15 min), the HA sintered by microwave were characterised by a density relatively higher than that of sintered by conventional furnace. For example, at 1100 °C the bulk densities of samples using CS and MS were about 2.49 (for 120 min) and 2.93 (for 15 min) g/cm³, respectively. Furthermore, a near theoretical density (98.6%) was obtained when HA samples were sintered at 1200 °C for 15 min only but using the proposed MS, which was much higher than that (89.7%) of HA samples sintered at the same temperature for longer holding time (120 min). Besides this, the X-ray analyses have shown that heat-treatment, using these two processes, has led to HA decomposition into tricalcium phosphate and/or tetracalcium phosphate.

Keywords Biomaterials · Bone · Hydroxyapatite · Sintering · Microwave sintering · Phase decomposition

Introduction

Hydroxyapatite (HA: Ca₅(PO₄)₃OH) has been studied for many years as an implant material because it is similar to the major constituents (mineral parts) of bone and tooth [1]. In general, there are two main ways of producing HA, the first one is synthetic method [2–7] and the other one is from natural bone [8–11]. Because of the effectiveness (high) cost of bioceramics production using conventional sintering (CS), due to their higher sintering temperatures for longer holding times. Therefore, to overcome this drawback an alternative process so called Microwave Sintering (MS) was proposed.

MS of ceramics has gained much attention during the last decade. Reasons for the growing interest in the use of microwave energy include rapid heating, enhanced densification rate, decreased sintering active energy and improved microstructure [12–15]. MS has also the potential for energy and cost savings when compared with Conventional Sintering (CS) [12, 16, 17]. However, to be useful for the preceding interests, most microwave apparatus must include a heat generator so called susceptor, temperature measurement device and thermal insulation. These three main parts are of a great interest to start any successful study in the microwave processing domain [18]. On the basis of the above-mentioned advantages, HA has been also prepared by this modified MS.

As the supply of autologous tissue is limited and can lead to complications at the donor site and as allogeneic tissue bears the risk of infections and immune response, a variety of materials has been developed in the past to fill defect bone [9]. There are many kinds of materials which were applied for filling such defects. However, among these materials, the most solicited for implantation is HA [19].

In this study, the HA powder material was prepared from calcined bovine bone at 800 °C, using both CS and

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MS in order to compare the effect of each kind of sintering on the stability and sinterability of HA.

Experimental procedure

Material

The HA powder was produced by calcination of bovine bone at 800 °C for 4 h followed by wet ball milling. The average particle size of the milled powder was about 1.0 μm. Afterwards, the powder was cold compacted at 75 MPa. In order to study the effect of sintering temperature and sintering method (CS or MS) on density and stability of HA, the compacted samples were sintered for 2 h at different temperatures varied from 1050 to 1200 °C. Series of three samples have been, generally, prepared for each sintering temperature. In order to evaluate the bulk density, both micrometre and electronic balance have been used. The sample dimensions (Height: H and Diameter: D) have been measured within a precision ~ 10 μm, whereas the weight (W) precision was about 10^{-4} g.

Sintering techniques

Sintering was carried out under air in a 2.45 GHz, 850 W modified commercial microwave oven (LG MC-805 AY) (U.K.) [18, 20] and conventional (electrical) furnace (Nabertherm: LH 30/14) (Lilienthal, Germany).

Characterisation procedures

The calcium to phosphorous molar ratio and ionic concentration of trace elements were determined using inductively coupled plasma-optical emission (ICP-OES) spectrometer (ICP-OES) (SPECTRO Ciros Vision) (Karlsruhe, Germany). Phase compositions for samples sintered at different temperatures were identified by X-ray diffraction (XRD) (BRUKER, D8 ADVANCE) (Karlsruhe, Germany) with a Cu K_{α} radiation ($\lambda = 0.154$ nm) and Ni filter, working voltage 40 kV and working current 30 mA.

Moreover, XRD technique was also used in order to determine the percentages of phases formed during samples sintering. In fact, these percentages were determined, using the following relations:

$$C(\text{HA}) = \frac{I(\text{HA})}{I(\text{HA}) + I(\text{TCP}) + I(\text{TetCP})}$$

$$C(\text{TCP}) = \frac{I(\beta - \text{TCP})}{I(\text{HA}) + I(\text{TCP}) + I(\text{TetCP})}$$

$$C(\text{TetCP}) = \frac{I(\text{TetCP})}{I(\text{HA}) + I(\text{TCP}) + I(\text{TetCP})}$$

where HA, TCP and TetCP are hydroxyapatite, β or α -TCP and $\text{Ca}_4\text{O}(\text{PO}_4)_2$, respectively.

It should be mentioned that $I(\text{HA})$, $I(\text{TCP})$ and $I(\text{TetCP})$ were the intensities of the more intense peaks of hydroxyapatite, TCP and $\text{Ca}_4\text{O}(\text{PO}_4)_2$, respectively.

Afterwards, the equivalent total theoretical (ρ_{th}) density for any sample may be calculated from the following equation:

$$\rho_{\text{th}}(\text{total}) = C(\text{HA})x\rho_{\text{th}}(\text{HA}) + C(\text{TCP})x\rho_{\text{th}}(\text{TCP}) + C(\text{TetCP})x\rho_{\text{th}}(\text{TetCP})$$

where C is the phase percentage (%), deduced from the main peak intensities of the existing crystallized phases. The theoretical densities (ρ_{th}) of HA, β -TCP, TetCP and α -TCP were 3.147, 3.056, 3.072 and 3.102 g/cm³, respectively. This method was successfully used in other work [10].

Microwave setup

MS of HA samples was carried out in a modified domestic microwave oven 2.45 GHz, adapted for temperature measurements. To be heated, the samples were put into a special microwave setup configuration (Fig. 1) which was more detailed elsewhere [18].

Results and discussion

Chemical composition

The chemical composition obtained by ICP-OES spectrometer is shown in Table 1. Several elements such as Na, Mg, K, Zn and Sr coexist as minor constituents in calcined

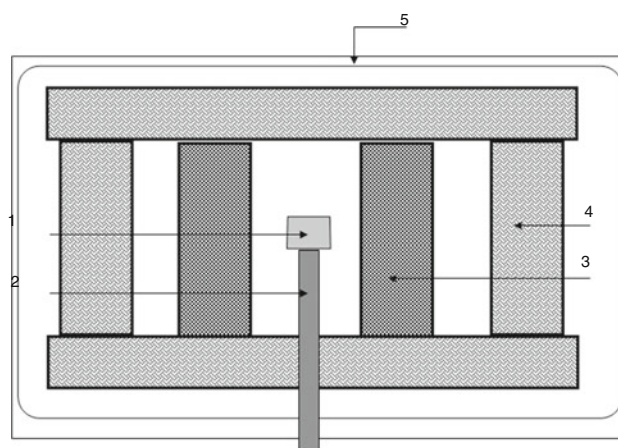


Fig. 1 Schematic diagram of the microwave set up configuration. 1 Sample, 2 Thermocouple, 3 Microwave heating element, 4 Thermal insulation, and 5 Oven cavity

Table 1 Chemical composition of bone calcined at 800 °C for 4 h, using ICP-OES spectrometer

wt%	Ca	P	Na	Mg	Sr	Zn	Fe	Si	K	Molar ratio/Ca × P ⁻¹
Calcined bone	37.0 ± 0.6	17.6 ± 0.3	0.781	0.705	0.042	0.006	0.050	0.002	0.069	1.63 ± 0.05

powder. This indicates that the bovine bone is not a pure HA; significant levels of additional trace elements are present within bone mineral [9, 11, 21, 22]. The calcined powder contains 37 and 17.6 wt% of Ca and P, respectively. These concentrations permit to obtain a molar phosphocalcic ratio (Ca/P) equal to 1.63 ± 0.05. These values are near to that of stoichiometric HA (Ca/P = 1.67) which contains 40.3 wt% Ca and 18.4 wt% P [23].

Conventional sintering

The X-ray diagram shows that the calcined powder is well crystallized (Fig. 2). It shows that HA (HA: Ca₅(PO₄)₃OH) is the only existing crystallized phase in calcined bone, according to JCPDS 09-0432. The same result was found in the literature [10, 11, 24].

The measured density of samples sintered at different temperatures is illustrated in Fig. 3. The existing phases were identified by X-ray diffraction; Fig. 4 shows the obtained results.

The unmarked peaks are attributed to HA phase

As would be expected, Fig. 3 shows that the bulk density increases with sintering temperature. In fact, the bulk density increases slowly between 900 and 1050 °C, where the density varies from 1.97 to 2.15 g/cm³. In contrast, this density increases sharply from 2.15 to 2.80 g/cm³, between 1050 and 1200 °C, respectively. Indeed, the variation in

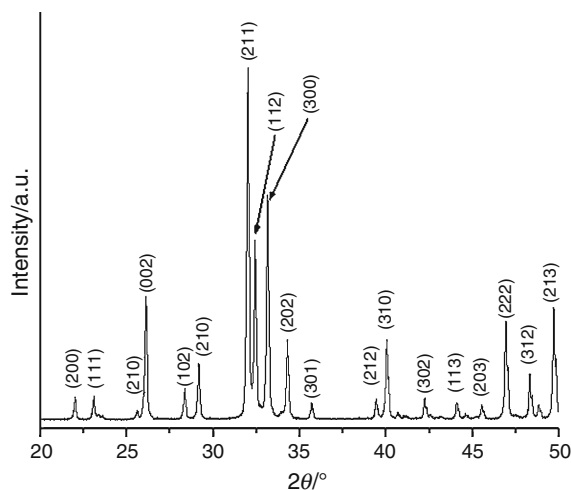


Fig. 2 X-ray diagram of bone calcined at 800 °C for 4 h

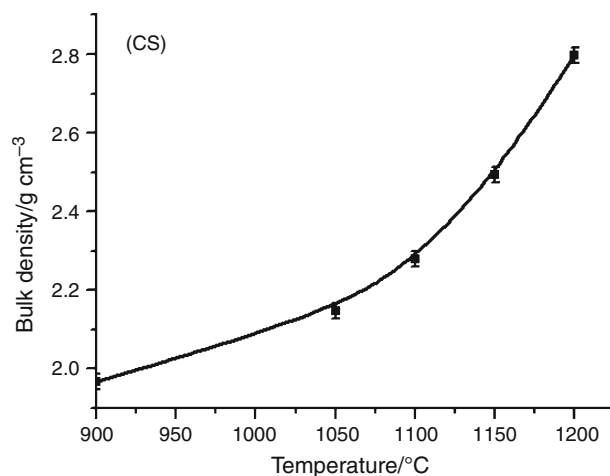


Fig. 3 Bulk density of HA sintered at different temperatures for 2 h, using CS

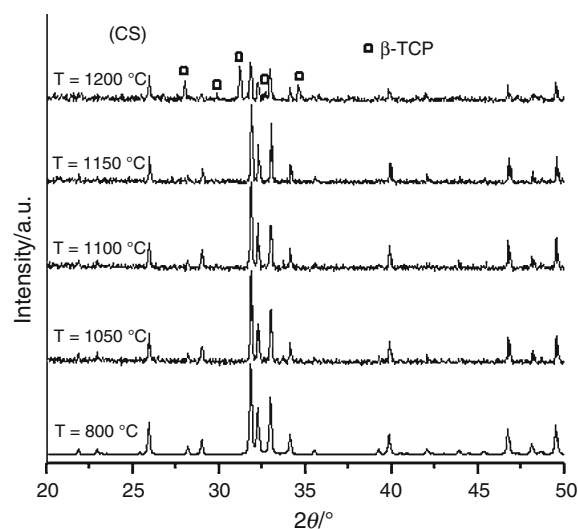


Fig. 4 X-ray diagrams of HA sintered at different temperatures for 2 h, using CS (open square (β-TCP) phase)

density value (0.16 g/cm³) in the first stage was lower than that in the second stage (0.65 g/cm³).

The X-ray analyses of samples using CS are illustrated in Fig. 4. These X-ray diagrams show that HA is stable until 1150 °C; the only existing phase is HA. However, at 1200 °C, X-ray diagram shows the presence of a second phase: β-tricalcium phosphate (β-TCP: Ca₃(PO₄)₂). The comparison of peaks intensity of these two phases may allow to conclude that about 50% of HA was decomposed into β-TCP.

These results are not, in fact, in contradiction with those reported by others [25–30]. It should be noted that the literature presents ambiguous data about the minimum decomposition temperature of HA during sintering. For example, the total absence of TetCP phase (Fig. 4) of natural HA decomposition may mainly due to its higher average particle size (1.0 μm). Therefore, it can be said that the coarser particles inhibits HA decomposition, using CS. This HA decomposition type was observed even at higher temperature (–1200 $^{\circ}\text{C}$). In contrast, their synthesised powders have a high sinter activity, resulting from the very small particle size (nanosized) and large surface area. Consequently, the HA decomposition into TetCP is encouraged.

Microwave sintering

When compared with CS there was a significant increase in density for samples sintered using MS. Since the MS took much shorter time (15 min), densification rate using MS may be considered to be higher than that of CS [25]. Nevertheless, it should be noted that HA decomposition still exist.

The density results and X-ray diagrams of samples sintered at different temperatures from 1050 to 1200 $^{\circ}\text{C}$ for 15 min, using MS, are shown in Figs. 5 and 6.

Figure 5 shows that the bulk density increases significantly from 2.62 g/cm^3 at 950 $^{\circ}\text{C}$ to 2.93 g/cm^3 at 1050 $^{\circ}\text{C}$. However, above 1050 $^{\circ}\text{C}$, the bulk density remains almost constant from 1050 to 1150 $^{\circ}\text{C}$. Afterwards, it starts to increase again with temperature which achieves 3.02 g/cm^3 at 1200 $^{\circ}\text{C}$. The sintered samples were investigated by X-ray diffraction in order to detect any phase transformation (Fig. 6).

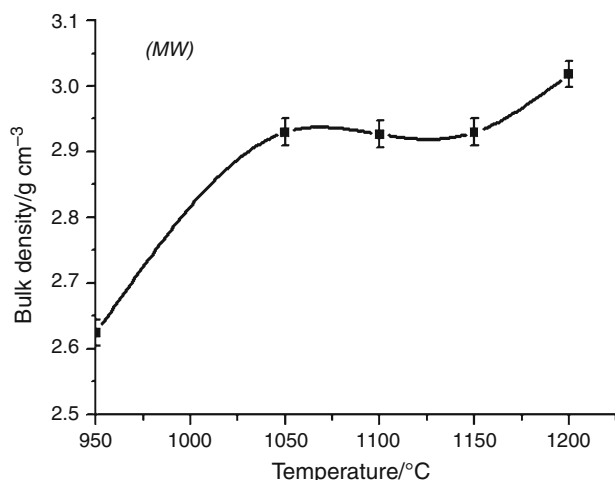


Fig. 5 Bulk density of HA sintered at different temperatures for 15 min, using MS

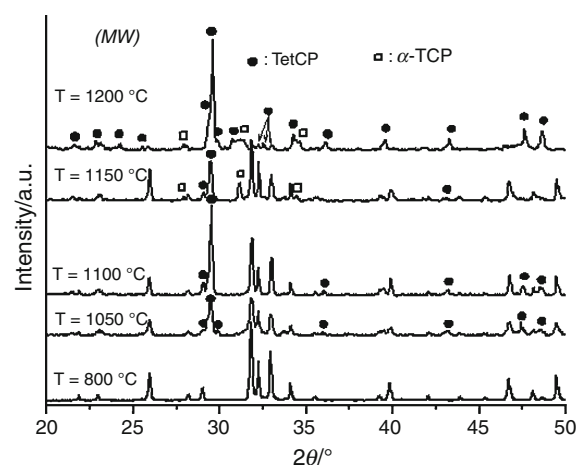


Fig. 6 X-ray diagrams of HA sintered at different temperatures for 15 min, using MS. (closed diamond $\text{Ca}_4\text{O}(\text{PO}_4)_2$ Phase, open square (α -TCP) phase)

The X-ray diagrams show the apparition of tetracalcium phosphate (TetCP: $\text{Ca}_4\text{O}(\text{PO}_4)_2$) phase in all specimens, using MS. The percentage of this phase was increased from 46 to 61% when the sintering temperature increases from 1050 to 1100 $^{\circ}\text{C}$, respectively. However, for samples sintered at 1150 $^{\circ}\text{C}$, the percentage of TetCP was decreased to about 33% as a result of α -TCP formation (16%). Afterwards, the percentage of TetCP phase restarted to increase again up to 85%, in samples sintered at 1200 $^{\circ}\text{C}$, within 10 and 5% of α -TCP and HA phases, respectively. It should be mentioned that these results are in good agreement with those reported by other workers [25–30]. Compared with conventional heating, the HA decomposition (using coarser powders) into TetCP and α -TCP phases and higher densities of the samples sintered by microwave heating were probably due to the higher heating efficiency of microwave heating.

For example, the existing phases in sample sintered at 1200 $^{\circ}\text{C}$ for 2 h, using CS, were HA and β -TCP within 53 and 47%, respectively. The corresponding theoretical density of this sample is

$$\begin{aligned} \rho_{\text{th}}(\text{total}) &= C(\text{HA}) \times \rho_{\text{th}}(\text{HA}) + C(\beta - \text{TCP}) \\ &\quad \times \rho_{\text{th}}(\beta - \text{TCP}) \\ &= 0.53 \times 3.147 + 0.47 \times 3.056 \\ &= 3.11 \text{ g}/\text{cm}^3 \text{ (relative density} = 89.7\%). \end{aligned}$$

Another example using MS, for sample sintered at 1150 $^{\circ}\text{C}$ for 15 min

$$\begin{aligned} \rho_{\text{th}}(\text{total}) &= 0.51 \times 3.147 + 0.16 \times 3.056 + 0.33 \times 3.072 \\ &= 3.11 \text{ g}/\text{cm}^3 \text{ (relative density} = 94.2\%) \end{aligned}$$

These 2 examples show that the theoretical densities are the same and much closer to that of HA, whereas the

corresponding relative densities were clearly different. Thus, it is a good example showing the MS effect. In contrast, the theoretical density using MS again, but for sample sintered at 1200 °C for 15 min is quite different (3.07 g/cm^3) (relative density = 98.6%). Therefore, a near theoretical density (98.6%) was obtained when HA samples were sintered at 1200 °C for 15 min only but using MS.

It should be mentioned that the unmarked peaks are attributed to the HA phase in Fig. 6.

The results illustrated in Fig. 6 confirm that there was a partial HA decomposition by formation of another phase at 1050 °C. According to ASTM files, this phase may be identified as TetCP. The intensity of the characteristic peaks of this phase increases, while the intensity of HA peaks decreases with MS temperature. Moreover, α -TCP phase is formed at 1150 °C in addition to TetCP. This may justify why the density remains stable between 1050 and 1150 °C. In fact, there is a competition effect between both sintering temperature and HA decomposition. The HA characteristic peaks disappeared at 1200 °C where both TetCP and α -TCP took place. That is why the density increased again.

Using MS, previous workers [31, 32] did not found a significant HA decomposition, contrary to the present work. This may be attributed to the difference in Ca/P ratio and trace elements or to sintering conditions (temperature, heating rate and sample dimensions).

Other studies [33, 34] showed that decomposition of HA into α -TCP and TetCP was accompanied by a water release. In this work, MS has led to HA decomposition into second phases (α -TCP and TetCP) more than when CS is used. The heat-treated samples by MS were smaller than those sintered using CS ($D_{MS} = 5 \text{ mm}$ and $D_{CS} = 13 \text{ mm}$); so the water release is more important in the first samples. Consequently, the decomposition occurs more in specimens sintered by microwave. It was mentioned that the greatest loss of water occurred during the initial stage of sintering before reaching the oxyhydroxyapatite maximum density [35]. At the same sintering temperature, samples sintered in microwave have density greater than that heat-treated in conventional furnace. As a result, the water is released in the first samples more than in the second samples; and consequently the decomposition process occurs more in the first samples.

Conclusions

The HA powder prepared from calcined bovine bone inherits some properties from its source and among these properties the Ca/P ratio and second phase which can be

decisive in phase formation during sintering. The comparison between the X-ray diagrams of sintered HA leads to conclude that sintering by MS lead to decomposition of HA into second phases (TCP and TetCP) more than when CS is used. Perhaps, the smaller dimensions of compacted sample dimensions have lead to HA decomposition more than that in samples obtained by MS.

It has been confirmed that the advantage of using MS is the rapidity of sintering (15 min) compared with CS. In fact, at 1100 °C the bulk densities of samples using CS and MS were about 2.49 (120 min) and 2.93 (15 min) g/cm^3 , respectively. Finally, a near theoretical density (98.6%) was obtained when HA samples were sintered at 1200 °C for 15 min only but using MS, which was much lower than that (89.7%) of HA samples sintered at the same temperature for longer holding time (120 min).

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